CHROME PYROPES FROM YAKUT DIAMONDS

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Chrome pyropes from Yakut diamonds

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The inclusion of minerals in diamonds, among which are often found garnets, have attracted the attention of scientists a long time ago. The first investigations concerning the determination of a_o values and N garnets (7) showed that they belong to the pyrone-almandine order. However, the insignificant quantity of these inclusions (0.05-0.3 mm) did not permit a study of their composition by analytical methods. Such investigations became possible only with the use of x-ray microanalyzers.

In the first work devoted to the study of chemical composition of garnets from African diamonds (18), four analyses of pyropes were presented which differed in composition from all known pyropes from the Kimberley tubes with insignificant lesser contents of CaO and an increased contents of Cr_2O_3. It was mentioned earlier (4), that the increase in garnets from kimberlites is connected only with the increase of Cr_2O_3 contents which is in view of their constant ferruginous nature. However, only the appearance of the first analyses permitted to reliably isolate a practically new group of pyrope garnets with a substantial content of $Mg_3Cr_2(SiO_4)_3$ admixture to 30%. This component was earlier assumed in garnets and was named hanleite (11), however later this name was recalled due to an incorrect garnet analysis from Henley, India (24). In recent years, a significant admixture of magnesium -chrome component (to 30%) independent from the results of garnet investigation in diamonds again demonstrated in garnets from kimberlite concentrates

of Africa. This final member was called knorringite (20).

In this work are presented results of the study of chemical composition of lilac garnets from Yakut diamonds. Diamonds from which garnets were extracted belong to type IIa (non-nitrous) (15) which was demonstrated by their infrared spectrum of absorption. In the infrared spectrum of separate samples there appears a system BI (1175 cm^{-1}) and also a 1365 cm^{-1} band (samples AO-90 AO-429) which are connected with defects of laminar diamond types (3).

Garnets extracted from diamonds differ in wide variations of the N value = 1.753-1.790. The garnet composition was determined by a x-ray micro analyzer MS-46 with accelerating pressures of 15 kilovolts. In the capacity of standards, the homogeneity of which was checked by micro-observation, diopside was used (for Mg, Si, Ca) with a composition close to a stoichometric one, pyrope (for Al, Fe) and a chrome-containing pyrope (for Cr) from xenolitic kimberlites of Yakut and also pure metals which included Ti and Mn.

Corrections were made for the measured correlations of intensities: for absorption by the Philiber method (22), taking into consideration the excitation potential of characteristic radiation of Heinrich (14) and by atomic numbers of Springer (27). Mass coefficients of absorption were calculated by the Heinrich tables (13). Since the composition of the samples and the standard were close, the correction for fluorescence was evaluated by Reed's method (23). This was insignificant and was not considered when these calculations were made.

As shown by the investigations conducted on the garnet samples, the reproduction of these measurements was characterized by the variation coefficient not exceeding 2% for a majority of the elements (with the exception of Ti and Mn) and only the determination of Mg was conducted with a certain

amount of error due to considerable absorption of its analytical lines in the thickness of the sample.

In Table 1 are presented results of 10 complete garnet analyses.

The results of the analyses corroborate the established principles of the examples of garnets from African diamonds (18) concerning particularly low CaO content and at the same time considerably widening the presentation concerning the introduction of the Cr_2O_3 admixture into their composition which is illustrated by the variation of Cr_2O_3 contents from 6.1 to 15.9%.

Table 1 Chemical analyses of garnets from Yakut diamonds

	АО-434	АО-460	АО-438	АО-449	АО-432	АО-90	АО-430	АО-456	АО-445	АО-458
SiO_2	42,7	42,6	42,7	42,5	41,7	41,4	42,5	41,0	40,4	41,4
TiO_2	0,02	0,02	0,02	0,02	0,03	0,02	0,03	0,02	0,17	0,08
Al_2O_3	18,0	17,9	18,4	18,2	17,6	17,0	16,8	16,6	13,2	11,1
Cr_2O_3	6,08	7,09	7,19	7,57	7,72	8,30	8,80	9,28	12,8	15,9
FeO *	6,02	6,93	6,55	6,34	7,01	7,28	6,85	7,09	6,15	6,18
MnO	0,21	0,28	0,28	0,21	0,37	0,28	0,37	0,31	0,30	0,23
MgO	23,4	22,6	23,3	24,0	22,5	21,4	23,3	21,7	23,0	23,1
CaO	1,33	1,24	1,09	1,94	1,46	2,38	2,22	2,32	2,33	2,24
1 Сумма	97,8	98,6	99,5	100,8	98,4	98,1	100,9	98,3	98,4	100,1
2 Пироп	67,7	66,9	64,9	64,9	62,0	59,2	59,5	57,4	47,5	38,7
3 Альмандин	8,6	12,0	11,6	10,7	12,9	13,7	11,1	13,9	9,4	8,9
4 Спессартин	0,5	0,6	0,6	0,4	0,7	0,6	0,7	0,6	0,6	0,4
5 Андрадит	3,6	3,3	2,7	2,7	2,1	2,2	3,9	1,1	5,0	5,8
6 Уваровит	—	—	0,2	2,2	1,8	4,2	1,7	5,0	1,2	0,1
7 Кохарит	2,2	0,1	—	—	—	—	—	—	—	—
8 Кнорринтит	17,4	17,1	20,0	19,1	20,5	20,1	23,1	22,0	36,3	46,1
9 Са-компонент	3,6	3,3	2,9	4,9	3,9	6,4	5,6	6,1	6,2	5,9
10 FeO/FeO+MgO**	9,0	12,5	13,9	11,3	13,5	14,8	11,9	14,9	10,1	9,5
11 *N* измеренное	1,753	—	—	1,757	—	—	—	1,767	1,780	1,790
12 *N* вычисленное	1,754	1,757	1,757	1,758	1,760	1,765	1,764	1,765	1,778	1,789

* All iron in the FeO form
** Without andradite calculation
1. Total
2. Pyrope
3. Almandine
4. Spessartine
5. Andradite
6. Uvarovite
7. Kocharite
8. Knorringite
9. Ca-component
10. FeO/FeO+MgO**
11. N measured
12. N calculated

Garnets with maximal contents of chromium, sample AO-458, consists of to 46% knorringite, which is considerably higher than its terminal contents determined up to this time in natural garnets. Simultaneously containing 40% pyrope, it is separated among other garnets of initial composition.

Since in all analyses there is fixed a certain defficiency of the total Al + Cr, the Fe part not exceeding 0.11, we considered as andradite (2-5.8%). The remaining Ca after calculation we join to uvarovite and the entire remaining Cr we recalculate for knorringite, the content of which varies from 17 to 46%. In the diagram of Figure 1, the knorringite contents are somewhat lower, since here the andradite component is not considered. Having the measured N values for the examined garnets, especially rich in knorringite, with conditions of additive properties we can calculate the N value for a theoretically pure knorringite. Such a calculation verified by a known analyses (20), gave the N value as 1.830, which is much lower than the known quantities from data of theoretical calculations (28). The recalculation of N values for the analyzed garnets with computation of values obtained by us of N for knorringite and data by synthetic end members of garnet orders (25) showed good concurrence factor (Table 1).

Besides data for Mg - Cr-garnet synthesis (10), recently there appeared information concerning the pyrope synthesis with an admixture to 20% of Mg-Cr components (2) with P = 50 to 60 k-bar and also data concerning N values for synthesized garnets. Calculation for pure knorringite by this data produces $N \cong 1.820$. The value of a_o obtained by approximate calculations by data (2) conform with the information in literature, that is $a_o = 11.620$.

As demonstrated by data presented in Table 1 concerning the contents of various components in garnets from Yakut diamonds, the above mentioned pyrope peculiarities from diamonds appear as clear typomorphic signs. Compared with the data for the average garnet composition from the ultra-basic rocks

(peridotites and kimberlites) (4) show that garnets from diamonds besides the marked peculiarities, differ with a lower ferruginosity (f) the lower quantity of which is noted for garnets from African diamonds (18).

The peculiarities of composition of the examined garnets are illustrated by the diagram in Figure 1, for which points of the garnet composition of kimberlite groups are plotted in that number from diamond and pyrope peridotites, which is known in basic occurrences by works (4, 9, 12, 19, 21) and by our unpublished data concerning the Cr and Ca cations in a crystal-chemical formula.

Garnets from diamonds form a separate field in the lower part of the diagram, differing from all known pyropes of low Ca composition. The field of possible garnet composition is separated (symbol 3) from certain African diamonds, with a certain higher content of calcium calculated by the values of the physical constant obtained from work (16). A low Ca content demonstrated that they relate to the olivine paragenesis, that is, garnets without pyroxene-wedges even in the kimberlites are obviously products of a greater, earlier crystalization. Nothing the peculiarities of the contents of these garnets, we cannot agree with a complete analogy of garnets from diamonds and garnets from kimberlite concentrates, based only on a high knorringite content (18, 20).

The separate field of the composition, which is in the direction of increasing the Cr content, with certain simultaneous increases of Ca contents, are formed by garnets from xenolitic peridotites in a paragenesis with olivine, enstatite and diopside and certain garnets from kimberlites. For garnets on the left side of the diagram with Cr_2O_3 contents less than 3-4%, the basic influence on the Ca content is shown by the various Na_2O contents in the associated pyroxene-wedges (5, 8). A significantly higher garnet

field from peridotites is found in points of garnets richer in calcium with an inclusion of chrome disthene (26) while intermediate conditions should be positioned by garnets from eclogites rich in chrome and without disthene (garnet analyses from concentrates).

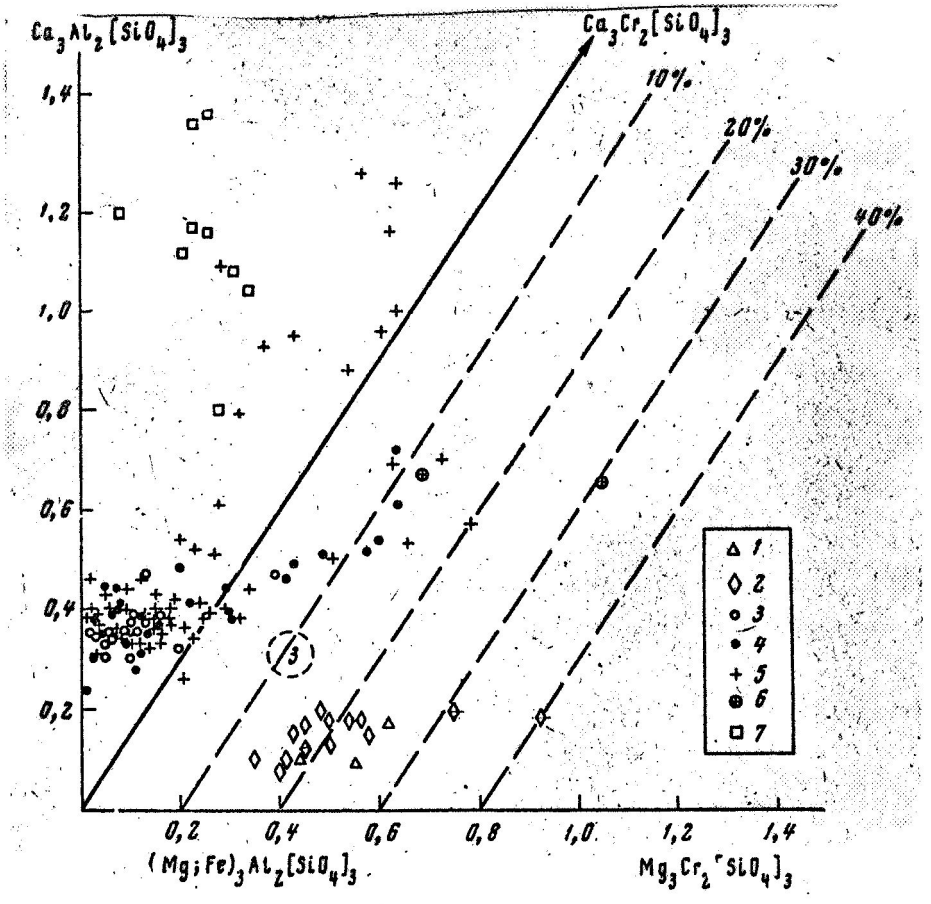

Figure 1 Garnet composition from ultra-basic rocks and kimberlites by Ca and Cr contents. 1. - Garnets from African diamonds; 2. - Garnets from Yakut diamonds; 3. - Garnets from peridotites known in a basic stratification; 4. - Garnets from xenolitic peridotites from kimberlites; 5. - Garnets from kimberlite concentrates; 6. - Garnets rich in knorringite from a kimberlite concentrates of Africa; 7. - Garnets with inclusion of chrome disthene.

In this way, chrome-containing pyropes and pyrope -- grossularite kimberlite garnet may be separated into four types of association: 1. Garnet + olivine + diamond, verified by frequent discoveries of olivine and pyrope in one and the same diamond as in the African one (16) and also in the Yakut lodes; 2. Garnet + olivine + enstatite + diopside; 3. Garnet + diopside; 4. Garnet + diopside + kyanite. In all of the indicated associations chromite may be present.

As seen in the diagram of Figure 1, the examined garnets from diamonds sharply differ with garnets from peridotites. Moreover, up to the present time they are not found in kimberlite concentrates. The latter may be partially connected with a deficiency of special investigations of the concentrate. Undoubtedly, in the latter, garnets surpass garnets of other types, namely pyropes of the usual peridotite garnet. Possibly this is due to the absence of a direct correlation between the quantity of the pyrope and the diamond content. Accordingly, the garnet quantities which crystalize simultaneously with the diamond are rather insignificant and only detailed examination of a larger quantity of pyrope concentrates in particular pyropes with an increased N value (more than 1.750) can resolve this question.

All the above mentioned relates to the Cr-containing pyropes with a characteristic violet, lilac and violet-pink hue. Along with that, there are known orange garnets in diamonds which according to the latest data (17) do not contain chromium and differ by an increased ferruginosity. They are close in composition to certain garnets of diamond bearing eclogites.

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